

Review

Emerging poly- and perfluoroalkyl substances in the aquatic environment: A review of current literature



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Poly- and perfluoroalkyl substances (PFASs) comprise a group of synthetic organic surfactants with a wide range of industrial and commercial applications. A few PFASs such as perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are now known to be ubiquitously present in the aquatic environment. They have become a global concern because of the toxicity and bioaccumulative properties. With the increasing availability of high-resolution mass spectrometers, many novel PFASs have been identified. Studies published between 2009 and 2017 have discovered 455 new PFASs (including nine fully and 446 partially fluorinated compounds), 45%, 29%, 17% and 8% of which are anions, zwitterions, cations, and neutrals, respectively. They have been identified in natural waters, fish, sediments, wastewater, activated sludge, soils, aqueous film-forming foams, and commercial fluoropolymer surfactants. This article integrates and critically evaluates what is known about these newly identified PFASs. It discusses the different aspects of detection methodologies. It also surveys the removal of these compounds during conventional and advanced drinking-water and wastewater treatment, predicts the relevant physicochemical properties by means of four software programs, and identifies major knowledge gaps. Notably, a number of these newly identified PFASs are potential precursor compounds of PFOS and PFOA. Studies are critically needed to understand the removal and transformation of these compounds in natural and engineered environmental systems and their contribution, if any, to the secondary formation of PFOS and PFOA in these systems.

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1. Introduction

Poly- and perfluoroalkyl substances (PFASs) are synthetic organic surfactants with a wide range of industrial and consumer applications. The fluorinated alkyl chain gives PFASs unique properties, including superior surface-tension-lowering properties and resistance to thermal and chemical degradation, which are absent in conventional surfactants (Kissa, 2001). These extraordinary properties allow for a wide range of applications beyond those of conventional surfactants. PFASs have been mass-produced since the 1950s and used as constituents of polymers in food containers, processing aids for nonstick cookware, surface-active agents in waterproof clothing and stain-resistant carpets, as well as ingredients in aqueous film-forming foams (AFFFs) and painting materials (Paul et al., 2009; Prevedouros et al., 2006). However, as is often the case with industrial chemicals, PFASs do not remain solely in their intended places. Once released to the natural environment they are not readily decomposable by physical, chemical, and biological mechanisms because of the strong carbon-fluorine bond (Eschauzier et al., 2012; Schröder and Meesters, 2005; Takagi et al., 2011). The widespread occurrence of PFASs in the environment, coupled with their known adverse health effects on humans, has caused great concern among the scientific community and the public (Blum et al., 2015; Giesy and Kannan, 2001; Prevedouros et al., 2006; Vestergren and Cousins, 2009).

Organic fluorine compounds were first detected in human serum in 1960s (Taves, 1966, 1968); however, this finding had not drawn considerable attention from the scientific community until the early 2000s, when a couple of anionic PFASs were found to be widespread in the environment and in wildlife (Giesy and Kannan, 2001; Hansen et al., 2002; Kannan et al., 2001a, 2001b, 2002a, 2002b; Martin et al., 2003; Moody and Field, 1999, 2000; Moody et al., 2002, 2003). Two long-chain, fully fluorinated compounds, perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3$) and perfluorooctanoate (PFOA, $C_7F_{15}COO$), have been measured in most of the components of the natural environment, such as polar regions where they have never been manufactured and used. It is generally accepted that they are persistent, bioaccumulative, ubiquitously present in the environment, and recalcitrant to removal by drinking-water and municipal wastewater treatment. These compounds have been measured in drinking water at numerous sites in the United States and in other parts of the world at concentrations ranging from a few to several tens of ng/L (Ericson et al., 2009; Eschauzier et al., 2012; Hoffman et al., 2011; Hölzer et al., 2008; Jin et al., 2009; Mak et al., 2009; Quinones and Snyder, 2009; Takagi et al., 2011). In May 2016, the U.S. EPA released updated drinking-water guidelines for PFOS and PFOA; the lifetime health advisory suggests a maximum combined level of 70 ng/L (USEPA, 2016). This updated advisory is certainly an important step toward reducing direct exposure to PFOS and PFOA via drinking water, although a lower advisory (1ng/L for PFOA) has been suggested earlier by selecting a different endpoint (Grandjean and Budtz-Jørgensen, 2013) (or see the summary of drinking-water advisories in (Xiao et al., 2015)). It should be noted that drinking water may be also contaminated by metabolizable precursor compounds of PFOS and PFOA, constituting an indirect source of exposure (Nabb et al., 2007; Tomy et al., 2004; Vestergren et al., 2008; Wang et al., 2009b; Yeung et al., 2013b). The significance of such indirect exposure can only be assessed after the identification of precursor compounds in drinking water.

2. Unidentified PFASs

On the basis of SciFinder search results as of June, 2017, more

than 4000 papers pertaining to PFOS and PFOA have been published since 2000 in English-language academic journals. These studies have greatly improved our understanding of the occurrence/concentrations, fate/transport/removal, and exposure/effects of PFOS, PFOA, and a few other legacy PFASs (Buck et al., 2011; Conder et al., 2008; D'eon and Mabury, 2011; Houde et al., 2011; Lau et al., 2007; Lindim et al., 2016; Martin et al., 2010; Paul et al., 2009; Post et al., 2012; Prevedouros et al., 2006; Rahman et al., 2014; Wang et al., 2013a; Xiao et al., 2013b; Yeung et al., 2013a). However, increasing evidence has shown that these legacy PFASs account for only a small fraction of the total organic fluorine present in the environment and wildlife. For example, unidentified PFASs account for 70e90% of organofluorine in seawater (Miyake et al., 2007), 15e70% of extractable organic fluorine (EOF) in human blood samples (Yeung et al., 2008), ~89% of EOF in shrimp (Loi et al., 2011), >56% of EOF in surface sediments (Yeung et al., 2013a), and >95% of EOF in surface soils (Tan et al., 2014). Most recently, Dauchy et al. measured the concentrations of 51 PFASs in a wastewater treatment plant (WWTP) receiving wastewater from a fluorochemical manufacturing facility. They found that unidentified PFASs account for 9e89% and 48e73% of the total adsorbable organic fluorine in WWTP influent and effluent samples, respectively (Dauchy et al., 2017).

Furthermore, compelling evidence has shown that PFOS and PFOA can be generated during biological wastewater treatment (Guo et al., 2010; Murakami et al., 2009; Schultz et al., 2006; Xiao et al., 2012). In one study, for example, the concentrations of PFOS, PFOA, and a few other PFASs increased significantly after municipal wastewater treatment (Xiao et al., 2012). A few non-ionic PFASs such as N-ethyl perfluorooctane sulfonamidoethanol (EtFOSE) and 8:2 fluorotelomer alcohol (FTOH) have been identified or proposed to be precursor compounds (Boulanger et al., 2005; Dinglasan et al., 2004; Rhoads et al., 2008; Wang et al., 2005a, 2005b). However, the yields to PFOS and PFOA are low (Dinglasan et al., 2004; Wang et al., 2005a, 2005b), for example, smaller than 1% after 4e10 d EtFOSE incubation in an activated sludge reactor (Boulanger et al., 2005; Rhoads et al., 2008). Another study reported a PFOA yield of only 2.1% after 28 d of 8:2 FTOH incubation in an activated sludge system (Wang et al., 2005b). Results from these studies suggest the presence of other unidentified precursor compounds that are readily biodegradable in WWTPs within a typical hydraulic retention time of a few hours (Guo et al., 2010; Murakami et al., 2009; Schultz et al., 2006; Xiao et al., 2012). Identification of these unknown precursor compounds is a pivotal step toward estimating the secondary formation of PFOS and PFOA from indirect sources (i.e., degradation of precursor compounds) and toward controlling the discharge of PFOS and PFOA from WWTPs to surface water and to possible drinking water sources.

3. Objectives of this review

With the increasing availability of high-resolution mass spectrometry (MS) systems, important progress has been made recently in the detection and identification of previously unknown PFASs including potential precursor compounds of PFOS and PFOA. These newly identified PFASs are referred as “emerging PFASs” as opposed to legacy PFASs (e.g., PFOS and PFOA). This paper reviews recent studies on the identification, occurrence, and fate of new PFASs in natural and engineered aquatic systems and identifies areas that merit further research. The fate of these compounds during conventional and advanced water treatment processes is reviewed. Calculated physicochemical properties of emerging PFASs using four software programs are discussed. This review is timely given the increased interest in emerging PFASs. It is hoped that the information provided in this review will improve our understanding

of this group of compounds in terms of their environmental behaviors and effects and aid in the development of effective treatment and remediation technologies.

4. Methods

Publications were searched primarily using the Scopus and Google Scholar databases. The studies that were reviewed include measurements of thousands of samples from several different countries. The compounds in this review include perfluoroalkyl sulfonates (PFASs), poly- and perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkyl phosphonic acids (PFPA), and new classes of partially fluorinated compounds. Between 2009 and 2017, studies have identified or proposed 455 novel PFASs, 45%, 29%, 17%, and 8% of which are anionic, zwitterionic, cationic, and neutral compounds, respectively (Table S1 of the Supplementary data). The predictions of physicochemical properties, namely, acid dissociation constant (pK_a), octanol-water distribution coefficient (K_{ow}), pH-dependent K_{ow} (or D) at pH 7, organic-carbon-normalized adsorption coefficient (K_{oc}), and Henry's Law constant (K_H), were made by using four programs, including two freeware (Marvin 15.10.26 and EPISuite 4.1) and two commercial software (ACD/Labs 12.0 and SPARC). The programs Marvin, ACD/Labs, and SPARC made reasonable predictions of pK_a of PFASs. The values of $\log K_{ow}$ and $\log D$ provide important information on the bioaccumulation potential and the treatability of an organic compound by adsorption-based technologies. They cannot be determined experimentally for PFASs because of formation of a third phase in addition to octanol and water. The predicted $\log K_{ow}$ and $\log D$ by ACD/Labs were unreasonably high in certain cases. Only SPARC and EPISuite could predict K_{oc} . The prediction made by SPARC was unreasonably high in most cases, which was thus not considered. K_H is an important parameter of the volatility of a particular compound and its removal potential by air stripping. It was predicted by SPARC and EPISuite. The aqueous solubility of organic compounds is important to consider when predicting or describing their transport in the aqueous environment and removal from water (Xiao et al., 2013a). The author found that all the programs significantly underestimated the solubilities of PFASs. It is a common approach to estimate the solubility from $\log K_{ow}$, which may underestimate the solubility of polar compounds, including many of the newly identified PFASs included in this review. Therefore, the results of predicted solubilities were not present.

5. Emerging fully fluorinated compounds

5.1. Cyclic PFASs

A novel, cyclic PFSA (perfluoroethylcyclohexane sulfonate (PFECHS), Table 1) was detected by De Silva et al. in water and fish from the Great Lakes (De Silva et al., 2011). The standard of PFECHS was purchased from Wako Chemicals (Richmond, VA, USA). This chemical was used as an erosion inhibitor in aircraft hydraulic fluids. It was present in 3M's F-98 surfactant that contained 66e70% PFECHS and 18e22% perfluoromethylcyclohexane sulfonate (PFMeCHS, Table 1) (De Silva et al., 2011). The production of PFECHS has been phased out since 2002 (De Silva et al., 2011). This cyclic PFAS likely has similar physicochemical properties as its linear counterpart (i.e., PFOS) (Table 1). The authors detected PFECHS at concentrations ranging from 0.16 to 4.35 ng/L in the surface water of the Great Lakes and from <MDL (method detection limit) to 2.5 ng/g ww in fish (De Silva et al., 2011). PFMeCHS was also detected in surface water at concentrations of <MDL to 0.42 ng/L that were semi-quantified by assuming an MS response equivalent to that of PFECHS.

In two recent studies, PFECHS was observed in herring gull eggs in the Great Lakes region at levels of ND (not detected) to 3.1 ng/g ww that, however, were much lower than those of PFOS (43.2e723 ng/g ww) (Letcher et al., 2015; Su et al., 2017).

Wang et al. observed PFECHS and perfluoropropylcyclopentane sulfonate (PFPCPeS; Table 1) in various samples of different matrices collected near the Beijing International Airport (Wang et al., 2016b). Their PFECHS standard was obtained from Chiron AS (Trondheim, Norway), which had been found to contain four isomers of PFECHS producing four adjacent liquid chromatograph (LC) peaks. The standard was also believed to contain PFPCPeS (Wang et al., 2016b). The PFECHS and PFPCPeS concentrations in surface water as measured by the authors were <MLQ (method limit of quantification) to 195.1 ng/L and <MLQe128.5 ng/L, respectively. The concentrations declined exponentially with increasing distance of the sampling points from the airport.

5.2. PFPA

PFASs, PFCAs, and PFPA are three major groups of anionic fluorinated surfactants. PFASs (e.g., PFOS) and PFCAs (e.g., PFOA) have been detected in the aquatic environment since the early 2000s. PFPA were first detected by D'Eon et al. in surface water and WWTP effluent in 2009 (D'Eon J et al., 2009). The concentrations of C6 perfluorohexyl phosphonic acid (PFHxPA), C8 perfluorooctyl phosphonic acid (PFOPA), and C10 perfluorodecyl phosphonic acid (PFDDPA) were quantified on the basis of the industrial product Masurf-780, which was calibrated further using authentic standards (D'Eon J et al., 2009). D'Eon et al. found that PFOPA occurred at 0.088e3.4 ng/L in surface water and at 0.76e2.5 ng/L in WWTP effluent samples (D'Eon J et al., 2009). PFHxPA and PFDDPA were also detected (D'Eon J et al., 2009). In the same study, PFOS/PFOA was found to occur at maximum concentrations of 31 and 180 ng/L in surface water and in WWTP effluent, respectively (D'Eon J et al., 2009).

In another study, D'Eon and Mabury reported the detection of C6/C6 and C6/C8 disubstituted PFPA (or perfluorophosphinic acids (PFPIAs)) at ~2 ng/g in WWTP sludge standard reference from the National Institute for Standards and Technology (D'Eon and Mabury, 2010).

Esparza et al. examined the levels of PFHxPA, PFOPA, and PFDDPA in surface water (n ¼ 10), sewage sludge (n ¼ 4), and sediment (n ¼ 4) samples from The Netherlands. These compounds were not detected in sewage sludge and sediments. Only PFOPA was found in one surface water sample (1 ng/L). In contrast, PFOS, a legacy PFAS, was measured at 3.3e25.4 ng/L in surface water, 0.007e1.9 ng/g dw in sediments, and 35e48 ng/g dw in sewage sludge (Esparza et al., 2011).

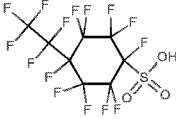

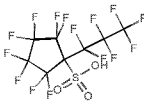
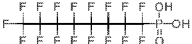
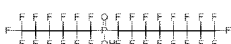

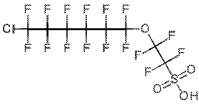


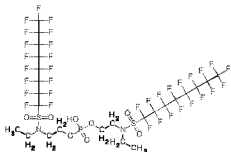
Ullah et al. determined the concentrations of three PFPA in tap water samples (n ¼ 7) collected from six countries (Ullah et al., 2011). Only PFOPA was detected at trace levels in two samples but below the MLQ. As a comparison, PFOS and PFOA at 0.397e8.81 ng/L and 0.302e8.56 ng/L, respectively, were detected (Ullah et al., 2011).

In a study by Kwok et al., no measurable PFPA (C6, C8, and C10) and PFPIAs (C6/C6, C6/C8, and C8/C8) were detected in seawater samples from Hong Kong (Kwok et al., 2015). PFOS and PFOA at 225.02e3642.50 and 702.93e2760.88 pg/L, respectively, were detected (Kwok et al., 2015).

Jin et al. reported results from a survey of 28 PFASs including the six PFPA and PFPIAs in samples of water (n ¼ 32), soils (n ¼ 27), and WWTP activated sludge (n ¼ 1) collected near a Chinese fluorochemical manufacturing park (Jin et al., 2015). PFOPA was detected in one WWTP effluent sample (1.11 ng/L) and in one soil (0.04 ng/g dw) (Jin et al., 2015). PFHxPA at concentrations of 0.41

Table 1

Physicochemical properties of a number of emerging PFASs predicted by SPARC (S), Marvin 15.10.26 (M), ACD/Labs 12.0 (A), and EPISuite 4.1 (E) and studies that first identified or proposed these emerging PFASs. The properties of four legacy PFASs (8:2 FTOH, EtFOSE, PFOS, and PFOA) were also presented as a comparison.

	pK _a	Log D (at pH 7)	Log K _{ow}	K _H (atm/mol/m ³)	Log K _{oc}	References
Emerging fully fluorinated compounds						
PFECHS	<1 (S) <1 (M)	3.81 (S) 2.35 (M) 1.68 (A)	5.08 (S) 4.73 (M) 5.18 (A) 4.42 (E)	7.12 ^L 10 ⁻⁵ (S) 1.22 ^L 10 ⁻³ (E)	3.37 (E)	(De Silva et al., 2011)
						
PFMeCHS	<1 (S) <1 (M) <1 (A)	2.61 (S) 1.65 (M) 0.78 (A)	3.90 (S) 4.03 (M) 4.28 (A) 3.45 (E)	6.03 ^L 10 ⁻⁶ (S) 2.33 ^L 10 ⁻⁴ (E)	2.83 (E)	(De Silva et al., 2011)
						
PFPCPeS	<1 (M) <1 (A)	2.09 (M) 0.13 (A)	4.47 (M) 3.63 (A) 2.74 (E)	1.22 ^L 10 ⁻⁶ (E)	2.44 (E)	(Wang et al., 2016a, b)
						
PFOPA	5.13 (S) 0.46 (M) 7.11 (M) 0.78 (A) 5.34 (A)	0.70 (S) 2.55 (M) 2.44 (A)	6.35 (S) 5.10 (M) 6.90 (A) 4.40 (E)	0.13 (S) 1.06 ^L 10 ⁻⁵ (E)	3.46 (E)	(D'Eon et al., 2009)
						
C6/C8 PFPIA	<1 (S) <1 (M) <1 (A)	9.79 (S) 8.94 (M) 13.35 (A)	12.58 (S) 11.20 (M) 16.85 (A) 8.30 (E)	1.66 ^L 10 ⁻⁶ (S) 5.38 ^L 10 ⁻² (E)	5.62 (E)	(D'Eon and Mabury, 2010)
						
Emerging partially fluorinated compounds						
HFPO-DA (GenX)	0.06 (S) <1 (M) <1 (A)	1.27 (S) 0.26 (M) 4.37 (A)	4.03 (S) 4.00 (M) 8.12 (A) 3.36 (E)	7.47 ^L 10 ⁻⁴ (S) 2.05 ^L 10 ⁻⁴ (E)	1.92 (E)	(Strynar et al., 2015)
						
6:2 Cl-PFAES (F-53B)	<1 (S) <1 (M) <1 (A)	3.03 (S) 3.51 (M) 6.22 (A)	4.84 (S) 5.88 (M) 9.72 (A) 5.24 (E)	2.76 ^L 10 ⁻⁴ (S) 1.71 ^L 10 ⁻⁵ (E)	3.73 (E)	(Wang et al., 2013a, b)
						
8:2 Cl-PFAES	0.14 (S) <1 (M) <1 (A)	5.41 (S) 4.91 (M) 8.00 (A)	7.26 (S) 7.29 (M) 11.50 (A) 6.58 (E)	4.24 ^L 10 ⁻² (S) 4.73 ^L 10 ⁻⁴ (E)	4.47 (E)	(Ruan et al., 2015)
						
6:2 FTAB	2.26 (S) NC (not calculable) (M) NC (A)	0.41 (S) NC (not calculable) (M) NC (A)	NC (not calculable) (M) NC (A) 0.9 (E)	3.82 ^L 10 ⁻¹⁵ (E)	0.71 (E)	(Moe et al., 2012)
						
SAmPAP diester	0.11 (S) 1.92 (M) 1.31 (A)	14.11 (S) 8.34 (M) 14.26 (A)	17.81 (S) 10.71 (M) 17.75 (A) 12.60 (E)	1.59 ^L 10 ⁻² (S) 3.51 ^L 10 ⁻⁵ (E)	8.23 (E)	(Benskin et al., 2012)
						

(continued on next page)

Table 1 (continued)


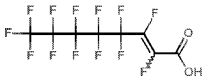





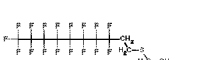
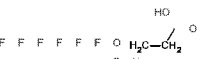
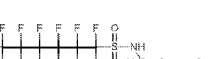
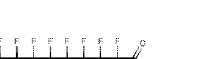



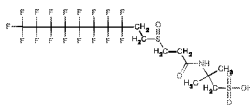
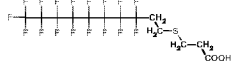
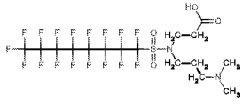
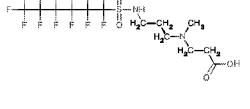
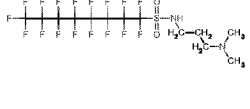
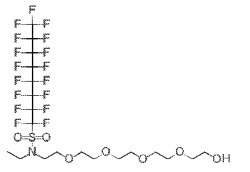

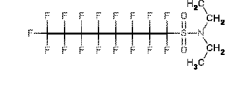

	pK _a	Log D (at pH 7)	Log K _{ow}	K _H (atm/mol/m ³)	Log K _{oc}	References
2HPFOA	<1 (S) <1 (M) <1 (A)	0.26 (M) 2.70 (A)	6.02 (S) 4.52 (M) 6.45 (A) 4.50 (E)	8.97 $\times 10^{-4}$ (S) 4.57 $\times 10^{-2}$ (E)	2.65 (E)	(Washington et al., 2015)
						
2uPFOA	<1 (S) <1 (M) <1 (A)	0.47 (M) 2.36 (A)	5.71 (S) 3.79 (M) 6.10 (A) 4.35 (E)	6.26 $\times 10^{-4}$ (S) 9.96 $\times 10^{-3}$ (E)	2.56 (E)	(Washington et al., 2015)
						
Cl-PFHxS	0.13 (S) <1 (M) <1 (A)	0.15 (S) 2.09 (M) 2.03 (A)	3.65 (S) 4.46 (M) 5.53 (A) 3.77 (E)	1.87 $\times 10^{-5}$ (S) 7.04 $\times 10^{-5}$ (E)	3.01 (E)	(Rotander et al., 2015)
						
Cl-PFOS	0.13 (S) <1 (M) <1 (A)	2.40 (S) 3.49 (M) 3.81 (A)	5.91 (S) 5.85 (M) 7.31 (A) 5.10 (E)	1.86 $\times 10^{-3}$ (S) 1.94 $\times 10^{-3}$ (E)	3.75 (E)	(Rotander et al., 2015)
						
Ether-PFHxS	0.13 (S) <1 (M) <1 (A)	0.025 (S) 2.82 (M) 3.67 (A)	3.44 (S) 5.20 (M) 7.17 (A) 3.91 (E)	2.76 $\times 10^{-5}$ (S) 6.20 $\times 10^{-7}$ (E)	3.00 (E)	(Rotander et al., 2015)
						
Ketone-PFOS	0.13 (S) <1 (M) <1 (A)	0.18 (S) 2.64 (M) 4.28 (A)	2.23 (S) 5.02 (M) 7.78 (A) 2.56 (E)	8.00 $\times 10^{-7}$ (S) 1.06 $\times 10^{-6}$ (E)	2.54 (E)	(Rotander et al., 2015)
						
Some novel PFASs found in AFFFs and surfactants						
8:2 FtSaAm	9.18 (S) 12.14 (S) 9.24 (M) 10.71 (M) 8.59 (A) 10.81 (A)	7.02 (S) 2.75 (M) 5.90 (A)	9.17 (S) 5.05 (M) 6.56 (A) 5.96 (E)	1.38 $\times 10^{-3}$ (S) 6.23 $\times 10^{-3}$ (E)	4.30 (E)	(Place and Field, 2012a, b)
						
8:2 FtAoS	0.36 (S) 11.97 (S) 1.05 (M) 12.05 (M) 0.70 (A) 15.42 (A)	1.85 (S) 3.62 (M) 2.20 (A)	6.05 (S) 6.00 (M) 5.70 (A) 4.41 (E)	1.29 $\times 10^{-11}$ (S) 2.14 $\times 10^{-10}$ (E)	3.34 (E)	(Place and Field, 2012a, b)
						
						
						
						
						
						
						

Table 1 (continued)

	pK _a	Log D (at pH 7)	Log K _{ow}	K _H (atm/mol/m ³)	Log K _{oc}	References
	<1 (S) <1 (M) <1 (A)	0.29 (S) 1.50 (M) 0.41 (A)	3.78 (S) 3.88 (M) 3.91 (A) 2.27 (E)	7.88 ^L 10 ¹⁷ (S) 1.35 ^L 10 ¹⁴ (E)	2.25 (E)	(D'Agostino and Mabury, 2014)
	4.34 (S) 3.59 (M) 4.33 (A)	6.12 (S) 3.51 (M) 4.93 (A)	8.76 (S) 6.86 (M) 7.56 (A) 7.04 (E)	0.01 (S) 1.19 ^L 10 ² (E)	4.05 (E)	(D'Agostino and Mabury, 2014)
	3.79 (S) 8.97 (S) 2.81 (M) 9.30 (M)	3.72 (S) 0.52 (M) 6.42 (A)	8.79 (S) 5.10 (M) 8.93 (A) 3.21 (E)	1.61 ^L 10 ⁵ (S) 7.66 ^L 10 ⁸ (E)	1.98 (E)	(D'Agostino and Mabury, 2014)
	3.47 (S) 6.49 (S) 3.52 (M) 9.43 (M) 7.18 (A) 9.50 (A)	0.91 (S) 3.67 (M) 3.69 (A)	6.13 (S) 3.47 (M) 6.37 (A) 1.66 (E)	2.32 ^L 10 ⁸ (S) 1.26 ^L 10 ⁹ (E)	1.15 (E)	(D'Agostino and Mabury, 2014)
	6.21 (S) 10.57 (S) 3.57 (M) 9.21 (M) 5.53 (A) 9.70 (A)	5.26 (S) 1.41 (M) 6.49 (A)	8.16 (S) 5.16 (M) 8.34 (A) 6.46 (E)	1.58 ^L 10 ² (S) 3.53 ^L 10 ³ (E)	4.57 (E)	(D'Agostino and Mabury, 2014)
	Neutral PFAS		4.75 (M) 7.50 (A) 4.90 (E)	3.34 ^L 10 ¹¹ (E)	2.98 (E)	(Xiao et al., 2017)
A few legacy PFASs 8:2 FTOH	Neutral PFAS		6.62 (S) 5.61 (M) 5.94 (A) 5.57 (E)	0.20 (S) 4.14 (E)	3.60 (E)	
	Neutral PFAS		7.57 (S) 4.97 (M) 8.65 (A) 6.00 (E)	1.44 ^L 10 ² (S) 5.72 ^L 10 ⁴ (E)	3.95 (E)	
	<1 (S) <1 (M) <1 (A)	3.29 (S) 3.05 (A) 3.53 (A)	5.50 (S) 5.43 (M) 7.03 (A) 5.43 (E)	4.23 ^L 10 ³ (S) 1.10 ^L 10 ² (E)	3.41 (E)	
	<1 (S) <1 (M) <1 (A)	4.11 (S) 0.85 (M) 4.00 (A)	6.90 (S) 5.11 (M) 7.75 (A) 4.81 (E)	2.53 ^L 10 ³ (S) 9.08 ^L 10 ² (E)	2.82 (E)	

and 30.2 ng/L was detected in two water samples. C6/C6 PFPIA was observed in some water samples, but the concentrations were not reported. PFDPA, C6/C8 PFPIA, and C8/C8 PFPIA were not detected in any of the water samples. In the same study, PFOS/PFOA levels reached 3630 ng/L, 11.1 ng/g dw, and 538 ng/g dw, respectively, in water, soils, and activated sludge (Jin et al., 2015).

Guo et al. measured PFPAs and PFPIAs in sediments from the

Lake Ontario and three inland lakes (Guo et al., 2016). Quantifiable C6/C8 PFPIA was found in five of 35 samples at a maximum level of 0.013 ng/g dw. Levels of PFPAs and C8/C8 PFPIA were below MDLs. As a comparison, PFOS was detected at levels of up to 10.09 ng/g dw.

Low concentrations and detection frequencies of PFPAs and PFPIAs have also been reported in biomonitoring studies. De Silva

et al. determined the concentrations of PFPAs and PFPIAs in blood samples of fish, birds, and dolphins in the Great Lakes region. They did not detect PFPAs. C6/C6, C6/C8, and C8/C8 PFPIAs were found in all of the samples at concentrations of a few ng/g ww, which, however, were two to three orders of magnitude lower than those of PFOS (De Silva et al., 2016). In another study, Lee and Mabury measured PFPAs, PFPIAs, and phosphate diester of N-ethyl-perfluorooctane sulfonamide ethanol (SAMPAP diester) in fifty human blood samples obtained from Golden West Biologicals (Temecula, CA) and a human serum reference sample from the National Institute for Standards and Technology (Lee and Mabury, 2011). No measurable PFPAs and SAMPAP diester were detected. PFPIAs were detected at levels of <LOD e60.96 ng/L (or up to 0.061 ng/mL). As a comparison, PFOS and PFOA were detected at 0.14e119.56 ng/mL and 0.19e5.16 ng/mL, respectively (Lee and Mabury, 2011). The SAMPAP diester standard was synthesized by the authors (Lee and Mabury, 2011).

As predicted by the software, the log K_{ow} and log D values of PFPAs are similar to their sulfonyl counterparts (Table 1). The predicted pK_{a2} of PFPAs is 5.13e7.11; thus, the fully deprotonated species that carries two negative charges is expected to dominate at neutral pH. PFPIAs and SAMPAP are apparent to be highly hydrophobic (Table 1), suggestive of strong adsorption potential and low solubility in water. Therefore, sediment is likely an important sink for PFPIAs and SAMPAP in the natural aquatic environment. The removal of these compounds during drinking-water and wastewater treatment is potentially high by activated carbon and sludge adsorption/enmeshment. PFPIAs have predicted pK_a values of <1. EPISuite and SPARC both predicted that PFPIAs are highly volatile, which seems to be unlikely given their rather long alkyl chains. Lee and Mabury studied the sorption of PFPAs (C6, C8, and C10) and PFPIAs (C6/C6, C6/C8, and C8/C8) on seven soils (Lee and Mabury, 2017). The authors fitted the adsorption data with the Freundlich model. The Freundlich nonlinearity coefficient in most cases was in the range of 0.8e1.1. The mean soil water distribution coefficients increased from $10^{0.2}$ for PFHxPA to $10^{2.1}$ for C8/C8 PFPIA (Lee and Mabury, 2017). The authors also calculated retardation factors for PFPAs and PFPIAs, and concluded that PFPIAs are relatively immobile and can be attenuated by soils and sediments due to sorption (Lee and Mabury, 2017).

6. Emerging partially fluorinated compounds

6.1. Fluoroether sulfonic or carboxylic acids: PFOS and PFOA alternatives

Since the phase-out of the production of PFOS, PFOA and related compounds either voluntarily or via the Stockholm convention for PFOS or via the stewardship program for PFOA (EPA, 2017; Wang et al., 2009a), a number of poly- and per-fluoroether sulfonates or carboxylates have been manufactured and introduced to the market (Wang et al., 2013c, 2017). In these compounds, the fluorinated segments are connected by ether linkage(s). It remains unclear whether the ether linkages make them more labile to degradation.

6.1.1. 6:2 CI-PFAES (F-53B)

F-53B (CAS number: 73606-19-6) is the potassium salt of 6:2 chlorinated polyfluorinated ether sulfonate (6:2 CI-PFAES; CAS number of 756426-58-1 for the free acid form). F-53B has been produced for decades as a PFOS alternative (Wang et al., 2013c). It was first detected in environmental samples by Wang et al. in the influent (43e78 mg/L) and effluent (65e112 mg/L) of WWTPs receiving electroplating wastewater (Wang et al., 2013b). They detected PFOS at similar levels, with average concentrations of 74 and 54 mg/L in the influent and effluent, respectively.

6:2 CI-PFAES and analogues (8:2 CI-PFAES and 10:2 CI-PFAES) were also the focus of a study by Ruan et al. (2015). The authors detected 6:2 CI-PFAES in all municipal sewage sludge samples (n ¼ 56) collected from 20 Chinese provinces and municipalities at levels (up to 209 ng/g dw) similar to those of PFOS. 8:2 CI-PFAES was also frequently detected at concentrations ranging from ND to 31.8 ng/g dw. 10:2 CI-PFAES was detected at much lower levels (ND to 0.86 ng/g) and at a much lower detection rate (23.2%). The standards of 6:2 CI-PFAES and 8:2 CI-PFAES were purified in the laboratory from the mist suppressant product of F-53B. Since the standard of 10:2 CI-PFAES is not commercially available, the concentrations of this compound were semi-quantified on the basis of the instrumental response factor (Ruan et al., 2015).

Wang et al. reported results from a survey of PFASs in water samples collected at the mouths of Chinese rivers. F-53B was frequently detected at a maximum level of 78.5 ng/L in samples collected near metal-plating facilities (Wang et al., 2016a).

Gebbink et al. determined the concentrations of more than 35 PFASs in 24 liver samples of Greenland marine mammals. The target PFASs included 6:2 CI-PFAES, four PFASs, four mono-substituted polyfluorinated phosphate esters (monoPAPs), eleven disubstituted PAPs (diPAPs), and eleven PFCAs. 6:2 CI-PFAES was detected in 23 of the 24 samples at 0.023e0.27 ng/g ww (Gebbink et al., 2016). Although the levels were substantially lower than those of PFOS (93e1811 ng/g ww), the results strongly suggest that 6:2 CI-PFAES is bioaccumulative and that its precursor compound(s) or itself can undergo long-range transport to the Arctic environment from the sources. Additionally, monoPAPs and diPAPs were below the detection limits in all the samples.

The environmental monitoring results suggest a potentially widespread exposure to 6:2 CI-PFAES. Indeed, 6:2 CI-PFAES was among the PFASs detected in all serum samples (n ¼ 100) from pregnant women and umbilical cords in China, with concentrations (geometric mean: 0.8e2.3 ng/mL) only lower than those of PFOS and PFOA. 8:2 CI-PFAES was also frequently detected (Pan et al., 2017). A few frequently studied PFASs in the literature, N-methyl perfluorooctane sulfonamidoacetic acid, N-ethyl perfluorooctane sulfonamidoacetic acid, and diPAPs, were not observed in any of the blood samples. The authors also found that 6:2 CI-PFAES can transfer from mother to fetus. The exposure pathways for 6:2 CI-PFAES remain unknown. Because of its similar chemical structure to PFOS, 6:2 CI-PFAES may be also recalcitrant to removal during drinking-water treatment. Wang et al. found that F-53B is resistant to removal by advanced oxidation and wastewater treatment (Wang et al., 2013b). Both 6:2 CI-PFAES and PFOS are nonvolatile and have similar predicted log K_{ow} and log D values (Table 1). It has been reported that the median lethal doses for zebrafish are similar between F-53B (15.5 mg/L) and PFOS (17 mg/L) (Wang et al., 2013b). 8:2 CI-PFAES appears to be much more hydrophobic and bioaccumulative than are 6:2 CI-PFAES and PFOS.

6.1.2. HFPO-DA (GenX)

The ammonium salt of 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid (HFPO-DA; CAS: 13252-13-6) is a new alternative to PFOS/PFOA, which has a trade name of GenX (CAS: 62037-80-3). The production history and volume of GenX are unknown. One reference mentioned it has been produced since 2009 (Chemours, 2017). It was first detected in environmental samples by Strynar et al. from the Cape Fear River (Strynar et al., 2015). The detection was confirmed with the available authentic standard (Strynar et al., 2015). The authors also tentatively detected 11 other perfluoroalkyl ether carboxylic and sulfonic acids (Strynar et al., 2015). The identification strategies included searching for ion clusters with m/z values differing from each other by $\pm m/z$ 50 (CF_2) or 66 (CF_2O) (Strynar et al., 2015).

In another study, HFPO-DA was detected in drinking water from around a fluorochemical manufacturing facility in the Cape Fear River watershed (Sun et al., 2016). The levels of HFPO-DA were below the limit of quantification (LOQ) in the drinking water of two communities upstream of the facility but elevated (55e4560 ng/L) in the drinking water of a downstream community. As a comparison, the total drinking-water concentrations of PFOS and PFOA ranged from <LOQ to 447 ng/L in the upstream communities and from <LOQ to 55 ng/L in the downstream community. A few other mono- and poly-ether perfluoroalkyl ether carboxylic acids proposed by Strynar et al. (2015) were also found in this study (Sun et al., 2016); however, the structures were not confirmed because of the lack of authentic standards.

HFPO-DA has been detected in other countries as well, which should be related to the local production and application of GenX. In a large occurrence study by Heydebreck et al., HFPO-DA was found to occur at a maximum concentration of 3825 ng/L (detection rate of 76%) in the Xiaqing River System in China (Heydebreck et al., 2015a, b). This compound was also observed in the Lower Rhine River (EU) system at concentrations of up to 107.6 ng/L and at a detection rate of 17% (Heydebreck et al., 2015b). The concentrations of PFOS were below 5 ng/L in the Xiaqing River System (Heydebreck et al., 2015b), but those of PFOA and several other PFCAs were elevated, ranging from 38.07 to 723,713 ng/L for PFOA (Heydebreck et al., 2015b). The levels of the PFOS and PFOA were lower than 20 ng/L in the Lower Rhine River system in this study (Heydebreck et al., 2015b).

The predicted pK_a of HFPO-DA is less than 1 (Table 1), indicating that the deprotonated species dominates at circumneutral pH. This compound appears to be nonvolatile and highly soluble in water. Sun et al. surveyed HFPO-DA in a drinking-water treatment plant (Sun et al., 2016). According to the information given in the original study and the associated supplementary document (Sun et al., 2016), it seems that the raw water was treated through the following processes. The surface river water was pre-ozonated at an ozone (O_3) dose of 3.1 mg/L and then coagulated with alum at a dose of 43 mg/L. After coagulation and settling, the water was ozonated again at an O_3 dose of 1.3 mg/L. The ozonated water was then passed through a biological activated carbon filter and disinfected by medium-pressure UV lamps at a UV dose of 25 mJ/cm² and by chlorination at a dose of 1.26 mg/L as Cl_2 . The concentrations of HFPO-DA in the raw water and after each of the treatment processes were not tabulated but given in a figure in the study. It is apparent from the figure that the HFPO-DA concentration increased from ~420 ng/L (raw water) to ~500 ng/L (water after pre-ozonation). The authors suggested that the increase might be caused by the generation of HFPO-DA from precursor compounds (Sun et al., 2016). The concentration of HFPO-DA changed from ~500 to ~450 ng/L after coagulation and sedimentation (10% difference). Interestingly, the HFPO-DA concentration increased again from ~450 ng/L to ~530 ng/L (~18% increase) during secondary ozonation at an even lower O_3 dose. If the increase was caused again by the transformation of precursor compounds, then it indicates that the reaction between O_3 and HFPO-DA precursor compounds was incomplete during pre-ozonation when O_3 might have been largely consumed by natural organic matter and inorganic species (e.g., bromide). However, it is unclear whether the concentration increase of HFPO-DA after ozonation were simply due to analytical variation. The biological activated carbon filtration did not significantly remove HFPO-DA, but UV inactivation and chlorination together seemed to slightly lower the HFPO-DA concentration from ~530 to 470 ng/L. Overall, the data of this study (Sun et al., 2016) suggest that HFPO-DA is readily removed during conventional and advanced drinking-water treatment. However, more studies are needed to understand the fate of HFPO-DA under

different treatment conditions (e.g., different Cl_2 and O_3 dosages, pH, and CT values).

The identification of GenX/HFPO-DA in the Cape Fear River has caused great concern to the local community (CBSNews, 2017). The bioaccumulation potential and toxicity of GenX, however, have not been determined. The author of this review purchased the standard of HFPO-DA and found that it is readily soluble in water (solubility $>10^2$ mol/L). Its structure indicates that it could be much less bioaccumulative and toxic than PFOS and PFOA. The author is not aware of the detection of GenX in biological samples (e.g., fish).

6.2. PFASs in AFFFs and commercial surfactant products

AFFFs containing PFASs have been used since the 1970s by military and commercial airports to suppress fires. As a result, PFASs were released into the environment with AFFF-based fire suppressants during firefighting and training activities. One of the pioneering publications on environmental contamination of PFASs reveals high PFOA levels (up to several mg/L) in groundwater at U.S. air force bases after 7e10 years of AFFF application to the sites (Moody and Field, 1999). A few years later, similar levels were still observed (Moody et al., 2003). In Germany, anionic PFASs at up to several mg/L were found in groundwater associated with a history of AFFF application (Wilhelm et al., 2010). In the United Kingdom, high levels of PFOS (>10 mg/L) in groundwater (2008 and 2009 data) were associated with AFFF contamination during the 1990s (Atkinson et al., 2008). In Sweden, PFOS and PFOA in groundwater remained in high concentrations near an abandoned fire-training site where AFFFs were used 30 years ago (Filipovic et al., 2015). These studies suggest that PFASs released to soils with AFFF applications constitute an important source of groundwater contamination and that, importantly, the contamination often lasts for many years after the release. Similar observations have also been made in other types of contaminated sites, such as manufacturing and PFAS-bearing waste disposal sites (Xiao et al., 2015). It should be noted that the sources of PFOS and PFOA detected at these contaminated sites may include their precursor compounds that are transformed to PFOS and PFOA by soil microorganisms. Houtz et al. estimated that precursor compounds account for 41e100% of the total molar concentration of PFASs in archived AFFF formulations (Houtz et al., 2013). Identification and understanding of these degradable PFASs and their biotransformation patterns is essential to cost-effective management of PFAS-contaminated sites and to selection of appropriate remediation technologies.

Place and Field made the first step toward characterization of PFASs in AFFFs manufactured from 1984 to 2011 by various manufacturers (Place and Field, 2012a). AFFF samples were first analyzed by fast atom bombardment mass spectrometry. Ions in series characterized by differences in m/z 50 (eCF_2e) and m/z 100 (eC_2F_4e) were selected, which were believed to be PFASs produced by electrochemical fluorination (ECF) and telomerization, respectively (Place and Field, 2012a). The candidate ions were then analyzed by quadrupole-time-of-flight mass spectrometry (QToF-MS) to obtain structural information. The authors discovered 27 PFASs, including 6:2, 8:2, 10:2, and 12:2 fluorotelomer sulfonamide alkylbetaines (FTABs) (Place and Field, 2012b); 6:2 and 8:2 fluorotelomer sulfonamide amines (FTSaAms); and 6:2 and 8:2 fluorotelomer thioamidodisulfonates (FTTaOs). As shown in Table 1, FTABs are zwitterions, FTsaAms are essential cations, and FTTaOs are anions. It is known that there exist anionic, non-ionic, cationic, and zwitterionic types of surfactants; however, studies before this one have exclusively focused on anionic PFASs and a few non-ionic PFASs (e.g., 8:2 FTOH). The fate, transport, removal, and transformation of

cationic and zwitterionic PFASs remain poorly understood.

Identification of unknown PFASs in AFFFs was also the focus of a study by D'Agostino and Mabury (D'Agostino and Mabury, 2014). The authors used both weak anion-exchange and weak cation-exchange solid-phase extraction (SPE) cartridges to elute and separate PFASs in AFFFs via different solvents. The collected SPE fractions were analyzed by combustion ion chromatography to estimate the total organic fluorine levels. Only SPE fractions containing organic fluorine were selected for further analysis. This pretreatment approach could effectively minimize the interference from nonfluorinated compounds present in their samples. With three MS systems including QToF-MS and LCeMS/MS, the authors discovered 103 PFAS compounds in 12 novel and 10 infrequently reported PFAS classes having the numbers of perfluorinated carbons ranging from 3 to 15. A number of cationic and zwitterionic PFASs were identified. The structures of the PFASs proposed by D'Agostino and Mabury agree well with those proposed by Place and Field (2012a); however, D'Agostino and Mabury believed that the three PFASs previously identified as 6:2, 8:2, and 10:2 fluorotelomer thioether amidocarboxylic acids (Place and Field, 2012a) should be PFAS betaines. D'Agostino and Mabury employed several approaches to identify PFASs and to elucidate the structure, including the use of eCF_2e and $\text{eC}_2\text{F}_4\text{e}$ as marker fragments, mass defect filtering, and AFFF patent documents. The authors also synthesized a PFAS and confirmed one of the proposed compounds (D'Agostino and Mabury, 2014).

In another study, Field and coworkers developed an interesting method to separate their newly identified AFFF PFASs. Cation-exchange and anion-exchange guard columns were connected in series to a reverse-phase (C18) analytical column, and PFASs were thus separated in the LC system not only based on their hydrophobicity but also based on the sign of the charge (Backe et al., 2013). AFFF PFASs were semi-quantified by assuming a molar MS response equal to that of PFASs with available analytical standards. The concentrations of telomerization-based AFFF PFASs ranged from 24 to 11,000 mg/L. Certain telomerization-based PFASs, such as FTABs, FtSaAms, and FtTAoSs, were found in multiple AFFF formulations from different manufacturers, but PFOS was not detected. The levels of ECF-based PFASs reached up to 960 mg/L in 3M AFFFs manufactured from 1989 to 2001. PFOS and PFOA were also detected in ECF-based AFFFs at maximum levels of 15,000 and 170 mg/L, respectively. In 12 groundwater samples collected from two different U.S. military bases, FTABs, FtSaAms, and most other AFFF PFASs were not observed. Only the negatively charged FtTAoSs were detected in two of the 12 samples at a range of 86e6900 ng/L. On the other hand, PFOS and PFOA were found in all of the groundwater samples at 88e78,000 ng/L and 8.9e220,000 ng/L, respectively.

In another study, AFFF PFASs were not observed in the aquifer of a training site where AFFFs were used between 1970 and 1990 (Houtz et al., 2013). More recently, Higgins, Field and coworkers reported the discovery of 26 novel PFAS classes in commercial surfactant products including AFFFs, as well as another 14 novel PFAS classes in AFFF-impacted groundwater (Barzen-Hanson et al., 2017).

The notable absence of many AFFF PFASs in the AFFF-impacted aquifer is interesting. The transport of PFASs may be retarded in the vadose and saturated zones because of their adsorption on soil and aquifer solids and the considerably high solid-to-water phase ratio in the subsurface environment (Xiao et al., 2015). The transport retardation is presumably more significant for cationic and zwitterionic PFASs than it is for anionic PFASs because of the electrostatic interaction with the soil particle surface that is usually negatively charged. In one study, for example, the positively charged perfluorohexane sulfonamide amine was detected in AFFF-

impacted soils and in aquifer solids but not in groundwater (Houtz et al., 2013).

Biodegradation by soil microorganisms may also contribute to the disappearance of AFFF PFASs (Harding-Marjanovic et al., 2015). Liu and coworkers studied the soil aerobic biodegradation of two cationic PFASs, perfluorooctane sulfonamide quaternary ammonium salt and perfluorooctaneamido quaternary ammonium salt (Mejia-Avendano et al., 2016). The first compound was recently identified in AFFF (Barzen-Hanson et al., 2017) and a Fluorad brand surfactant (Xiao et al., 2017). The tertiary amines of both compounds were previously identified in AFFFs (D'Agostino and Mabury, 2014; Place and Field, 2012a). The soil biodegradation of the first compound was found to be much slower, yielding only 0.3% of PFOS on a molar basis. The second compound was found to degrade with a half-life of ~142 days and generate PFOA at a yield of 30% on a molar basis after 180 d incubation (Mejia-Avendano et al., 2016). In another study, Harding-Marjanovic et al. observed the complete degradation of 4:2, 6:2, and 8:2 FtTAoSs at initial concentrations of 0.005e26 mmol/L by soil microorganisms in 45 d of incubation (Harding-Marjanovic et al., 2015). Weiner et al. found that 6:2 FtTAoS was readily biodegradable during WWTP activated sludge treatment, leading to the formation of 6:2 FTOH and a couple of short-chain PFCAs (Weiner et al., 2013).

Perfluorooctane sulfonyl fluoride (POSF) is generally believed to be the building block of AFFFs and surfactants produced by 3M. AFFFs account for only less than 10% of the total POSF production volume (~96,000 t between 1970 and 2002 (Paul et al., 2009)). POSF was (mainly) employed before 2002 as the starting chemical to manufacture substances in several mainstream fluoropolymer products including Fluorad brand surfactants used in household chemicals, insecticides, and chemical intermediates (3M, 1999a, b, Kissa, 2001). The identities of PFASs in these commercial surfactants are largely unknown in comparison with the PFASs identified in AFFFs (Barzen-Hanson et al., 2017; D'Agostino and Mabury, 2014; Place and Field, 2012a). Such information would be useful for estimation of historical occupational, customer, and environmental exposures to PFASs from the production and application of these surfactants. The author of this review recently developed a new non-targeted PFAS identification approach based on the high-resolution precursor ion search (HRPIS) on a ToF-MS capable of performing continuously interleaving scans at low and high collision energies (ToF-MS^E) (Xiao et al., 2017). In that study, the hypothesis that PFASs can be detected by the ToF-MS^E HRPIS of their characteristic fragments was confirmed with 24 certified PFAS standards. This innovative method was then applied to five Fluorad brand surfactants, leading to the identification of 47 new and 43 infrequently reported PFASs including 40 non-ionic, 30 cationic, 15 zwitterionic, and five anionic compounds (Xiao et al., 2017). Most of the 38 infrequently reported PFASs were only recently identified in AFFFs in an earlier study (Barzen-Hanson et al., 2017). The results suggest that certain PFASs might have been used in multiple applications, meaning that a PFAS present in AFFFs may also be found in a surface treatment surfactant. Two of the five Fluorad brand surfactants (Xiao et al., 2017) were also previously analyzed by Barzen-Hanson et al. (2017). It is worthy to mention that a couple of PFASs identified in one study were not observed in another study (Xiao et al., 2017), which may be caused by the change of formulation of the surfactants by their manufacturer or different identification methods used in these two studies.

6.3. Cationic and zwitterionic PFASs

A significant number of the newly identified PFASs in AFFFs and commercial surfactants are cationic and zwitterionic compounds. Little is known about their physicochemical properties, effects, and

removal from water in comparison with legacy, anionic PFASs (e.g., PFOS and PFOA). 6:2 FTAB, a zwitterionic PFAS found in AFFFs and commercial surfactants (D'Agostino and Mabury, 2014; Moe et al., 2012; Place and Field, 2012a), has been frequently observed in environmental samples. Boiteux et al. reported results of a survey of 29 PFASs, including 6:2 FTAB in water, sediment, and soil samples collected around an active AFFF-applied fire training site (Boiteux et al., 2016). Surface water and sediment samples were collected from a river receiving wastewater from the training site. 6:2 FTAB was the predominant PFAS in surface water and sediment samples upstream of the wastewater discharge point, occurring at maximum levels of 140 ng/L in water and 8 ng/g dw in sediment. The concentrations of other 28 target PFASs, including PFOS and PFOA, were below LOQs. The levels of 6:2 FTAB increased to 17,874 ng/L in surface water and to 81 ng/g dw in sediment samples downstream of the wastewater discharge point. The levels were much higher than the other PFASs (e.g., 226 ng PFOS/L and 57 ng PFOA/L in surface water). 6:2 FTAB was also detected in soil samples collected from two active fire training areas at 494e4873 ng/g dw, which is 3e7 and 62e180 times greater than the those of PFOS and PFOA, respectively. No measurable PFASs, including 6:2 FTAB, were detected in a soil sample collected from a historical fire training site.

Dauchy and coworkers conducted surveys of PFASs in the aquatic environment near a fluorochemical manufacturing facility. In one study (Boiteux et al., 2017), the authors reported the detection of 6:2 FTAB in a river near an industrial WWTP receiving wastewater from a fluorochemical manufacturing site. They collected river water samples in May, July, October, and December in 2013. 6:2 FTAB was measured only in December samples at levels much higher than those of the other target PFASs. The concentration decreased from 968 ng/L near the WWTP to 248 ng/L at ~62 km away from the WWTP discharging point. The authors also studied the removal of 6:2 FTAB during different treatment processes. It seems that the removal of 6:2 FTAB by coagulation and sand filtration was poor, whereas ozonation and nanofiltration could reduce the concentration of 6:2 FTAB below the LOQ (25 ng/L). However, the concentration of 6:2 FTAB in the nanofiltration concentrate was as high as 2248 ng/L and thus probably required further treatment (Boiteux et al., 2017). The authors in another study also reported the measurement of 6:2 FTAB in the influent at 3987e45,462 mg/L and the effluent at 7074e14,558 mg/L of the above-mentioned industrial WWTP (Dauchy et al., 2017).

Munoz et al. detected 6:2 FTAB at 0.023e3.9 ng/g dw (semi-quantified) in sediment samples (n = 12) collected across France (Munoz et al., 2016). A cationic PFAS, 6:2 FtSaAm, was found to occur at 0.0092e6.1 ng/g dw. Their analogues, 8:2 FTAB and 8:2 FtSaAm, were also frequently detected. PFOS and PFOA were observed at maximum levels of 23 and 1.3 ng/g dw, respectively (Munoz et al., 2016). Most recently, Munoz and coworkers detected 8:2 FTAB, 10:2 FTAB, 6:2 FtSaAm, 8:2 FtSaAm, and a couple of other recently discovered PFASs (D'Agostino and Mabury, 2014; Place and Field, 2012a) in sediment and fish samples following the use of AFFF concentrate in response to an accidental crude oil release (Munoz et al., 2017).

Moe et al. studied the photolytic transformation of 6:2 FTAB after exposing the compound to UV light for 96 h at 1 °C and for 180 h at 15 °C (Moe et al., 2012). A UV lamp simulating sunlight in the UVA region (295e365 nm) was used. No measurable decline in 6:2 FTAB was observed. Several transformation products were observed but not quantified because of the lack of authentic standards. The authors also studied the in vivo transformation of 6:2 FTAB by exposing blue mussels and turbot to the chemical at 0e1000 mg/L for 96 h and at 0e250 mg/L for 48 h, respectively. 6:2 FTAB was readily metabolized and several major metabolites were

detected (Moe et al., 2012). PFOS and PFOA were not among the metabolites.

Probably because of the permanent positive charge, the physicochemical properties of 6:2 FTAB cannot be predicted by programs other than EPISuite. EPISuite predicts that 6:2 FTAB is nonvolatile and slightly hydrophobic (log K_{ow} \approx 0.9). Its solubility in water is likely high given the multiple polar functional groups. The log K_{ow} and log D values of FtSaAms predicted by Marvin and EPISuite appear to be in the reasonable range (Table 1). The predicted $pK_{a,1}$ of 6:2 FtSaAm is 8.58e9.24 (Table 1), which suggests that its positively charged species dominates at neutral pH and the neutral species can dominate under mildly alkaline conditions.

6.4. Other novel PFASs

Benskin et al. reported the detection of SAMPAP diester in sediment samples at concentrations of 40e200 pg/g dw (Benskin et al., 2012). This compound was a major component of 3M FC-807 that contains 30% (w/v) SAMPAP diester.

Baygi et al. developed a screening algorithm that can search for novel PFASs (Baygi et al., 2016) based on the EPA's Great Lakes Fish Monitoring and Surveillance Program. Their results suggest the presence of 30 novel, highly unsaturated PFASs that were not previously reported. However, the chemical structures of the 30 proposed PFASs were not confirmed.

Using LC coupled to an ultrahigh resolution Orbitrap MS, Liu et al. found 36 new PFASs in five classes in wastewater from a fluorochemical manufacturing plant (Liu et al., 2015). In their study, LCeMS in-source fragmentation scans were used to search for PFASs producing diagnostic fragments. The candidate compounds were then analyzed by MS/MS and Orbitrap MS to obtain the molecular formula and structural information. However, the chemical structures of these new PFASs could not be confirmed because of the lack of authentic standards.

Newton et al. recently discovered nine PFCAs, each differing by CF_2CH_2 , in surface water of the Tennessee River near PFAS manufacturing facilities in the Decatur area (United States). These nine PFCAs were not found in sediment samples (Newton et al., 2017).

Washington et al. found 22 unsaturated (2uPFCAs) and 2H (2HPFCAs) PFCA homologous series in sludge-applied soil and grass samples (Washington et al., 2015). Two of them (2uPFOA and 2HPFOA) were confirmed using authentic standards obtained from Wellington Laboratories (Guelph, Canada) (Washington et al., 2015). 2uPFCAs and 2HPFCAs have structures similar to those of their fully fluorinated counterparts, but 2uPFCAs have a double bond between a and b carbons and 2HPFCAs have a H substitution of F on an a carbon. Their results show that 2uPFCAs and 2HPFCAs were widespread in sludge-applied soil samples (Washington et al., 2015). The authors also performed soil degradation experiments using 2uPFOA, 2HPFOA, 8:2 fluorotelomer acid, and 8:2 FTOH. They found that 2uPFOA and 2HPFOA are biodegradation products of 8:2 fluorotelomer acid and suggested modifications to 8:2 FTOH biodegradation pathways proposed by other investigators (Washington et al., 2015).

Rotander et al. employed a case-control approach for identifying PFASs in the blood sera of firefighters (Rotander et al., 2015), which may be applied to environmental samples. In their method, blood sera samples were collected from firefighters and from a control group of people who had not been exposed to AFFFs. The samples were analyzed by LCeQToF-MS/MS. The peaks/ions were analyzed by multivariate statistical methods including principle component analysis. Ions strongly associated with firefighters were then analyzed again by LCeQToF-MS/MS to obtain the structural information. The authors tentatively identified four novel PFASs, 1-

chloro-PFOS, ketone-PFOS, ether-PFHxS, and 1-chloro-PFHxS. The authors proposed the position of chlorine in 1-chloro-PFOS on the basis of comparison of its MS spectra with those of 8-chloro-PFOS (Rotander et al., 2015). Nevertheless, an unequivocal identification of these four novel PFASs could not be made as their standards were not available. Their predicted pK_a values are <1 (Table 1); 1-chloro-PFOS is slightly more hydrophobic than PFOS, which, in turn, is slightly more hydrophobic than ketone-PFOS (Table 1).

7. Conclusion

Emerging PFASs will remain a moving target as novel PFASs are continuously being identified. This article reviews the advances in detection, characterization, and removal of emerging PFASs during drinking and wastewater treatment. The author made every attempt to include new PFASs that have been identified or proposed as of June 2017. Three new classes of fully fluorinated compounds (cyclic PFASs, PFPAs, and PFPiAs) have been identified in environmental samples. A larger amount of partially fluorinated PFASs have been proposed or identified, and a few of them (2uPFOA, 2HPFOA, SAMPAP diester, GenX/HFPO-DA, F-53B/6:2 Cl-PFAES, and 6:2 FTAB) have been confirmed in cases where the standards or commercial surfactant products are available. Many of the PFASs found in AFFFs and commercial surfactants are derivatives of perfluorooctane sulfonamide or fluorotelomer sulfonamide, in which the amine group is bonded to various nonfluorinated moieties, including betaines. But some have unusual structures (Barzen-Hanson et al., 2017; D'Agostino and Mabury, 2014); it remains unclear whether they are the major components in the AFFFs and surfactants or just manufacturing impurities. In addition, inconsistency has been found between different studies (Barzen-Hanson et al., 2017; Xiao et al., 2017) on the identification of PFASs in surfactants. It may be due to the formulation change of the surfactants or due to the different analytical methods. Interlaboratory studies are recommended.

Major knowledge gaps exist with regard to the behavior, fate, and effects of these newly identified PFASs in various parts of the urban water cycle, including municipal wastewater, rivers, urban lakes, drinking water, stormwater, and groundwater. There is insufficient literature documenting the fate of these compounds during conventional, enhanced, or advanced drinking-water treatment and the pathways of exposure to humans. Detailed removal studies are needed with respect to the effects of the solution chemistry, dosages of chemicals, and co-contaminants. Many potential precursors of PFOS and PFOA have been identified. However, the literature is still insufficient to draw a confident conclusion on the contributions of precursor compounds to the secondary formation of PFOS and PFOA in both natural and engineered environmental systems, such as WWTPs and AFFF-impacted sites.

Many of the newly identified PFASs appear to be nonvolatile, ionic or ionizable, moderately hydrophobic, and soluble in water (Table 1). Therefore, the aquatic environment is likely to be the ultimate sink for these chemicals. If released to soil, they may interact with soil organic matter and sorb to soil particles; however, they may also move off-site and reach surface water via runoff and groundwater via leaching. A major gap is the limited experimental data on the relevant physicochemical properties, including solubilities, soil-water distribution coefficients, K_{oc} values, as well as bioconcentration and bioaccumulation factors. This information will be useful for fate, transport, and exposure studies.

Numerous cationic and zwitterionic PFASs have been identified in AFFF and AFFF-contaminated sites (soil and groundwater). The sorption and desorption of cationic and zwitterionic PFASs on soils and aquifer solids have never been reported. Adsorption of anionic

PFASs on the mineral surface is known to be controlled by the hydrophobic effect and the electrostatic repulsion with the negatively charged surface (Higgins and Luthy, 2006; Tang et al., 2010; Wang and Shih, 2011; Xiao et al., 2011). Cations are electron acceptors. Previous adsorption studies on cationic and zwitterionic pharmaceuticals have indicated a cation-exchange mechanism (Carrasquillo et al., 2008; Figueroa et al., 2004). Cationic and zwitterionic PFASs may be attracted to the negatively charged soil particle surface by the exchange with previously adsorbed cations at anionic sites where they become stabilized by Coulombic forces. The sorption of cationic and zwitterionic PFASs to soils is potentially strong. Knowledge of their sorption and desorption behaviors in soil systems is needed to define soil quality criteria, develop remediation technologies, and establish standards for levels of acceptable contamination after remediation.

The sorption/desorption patterns (kinetics, thermodynamics, hysteresis) of cationic and zwitterionic PFASs may further control their bioavailability to soil bacteria. Many sites have been contaminated by PFASs for years or decades. The "aged" PFASs diffused into soil micropores may be less available for chemical and biological degradation. The magnitude of the resistant fraction may increase with aging in the environment as have been observed for legacy aromatic contaminants (see references in (Alexander, 1995)). One study (Mejia-Avendano et al., 2016) has shown that two cationic PFASs are biodegradable after spiking the chemicals to a soil microcosm, which is a common approach in PFAS biodegradation studies (Harding-Marjanovic et al., 2015; Weiner et al., 2013). It remains unclear if "aged" cationic or zwitterionic PFASs in a historical contaminated site are still readily biodegradable.

Furthermore, the IUPAC names of these newly identified PFASs can be obtained, for example, by using the Marvin software. However, there are inconsistencies in acronyms and terminology between different research groups. For example, FtTAoS and HFPO-DA in other studies have been named as FTSAS (D'Agostino and Mabury, 2014) and PFPPrPA (Sun et al., 2016), respectively. Harmonized acronyms and terminology for these emerging PFASs have not been established.

Lastly, a couple of PFASs (e.g., GenX and F-53B) have been manufactured as alternatives to PFOS/PFOA. The paucity of reliable data regarding their production, use, and disposal prevents the accurate determination of their quantities still in use and where they are used. A comprehensive and reliable inventory of global manufacture, use, and disposition of these alternative compounds should therefore be developed. These gaps represent the greatest needs of research into PFASs in the future.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2017.07.024>

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